

# APPARATUS AND METHOD FOR REMOVING ORGANIC POLYMER SUBSTANCE

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Inventor: ONO HITOSHI

Applicant: SHARP KK

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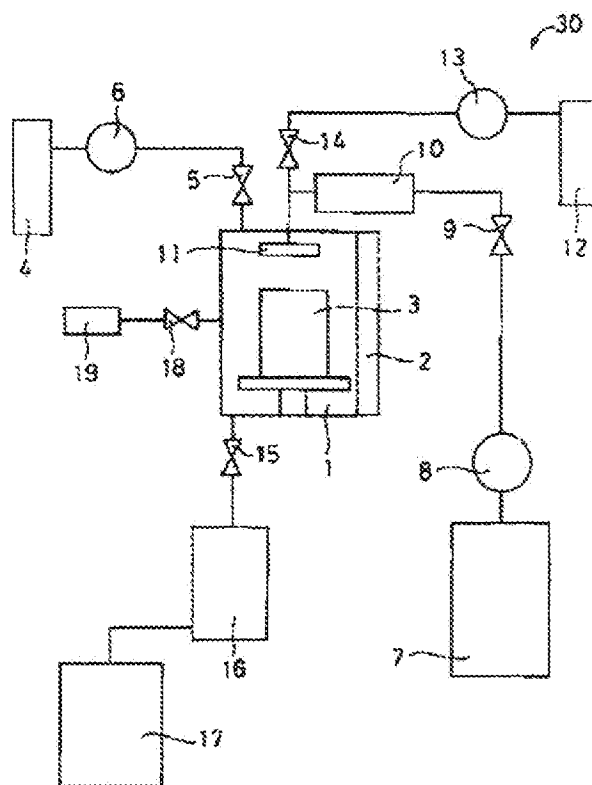
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## Abstract of JP2002343760

**PROBLEM TO BE SOLVED:** To provide the removing apparatus of organic polymer substances that can reduce tact time required for treatment without contaminating an object to be washed with metal and organic impurities or the like being eluted from a pressure resistant tank by fluid, when the organic polymer substances are removed from the object to be washed where the organic polymer substance adheres or welds, and to provide the removing method of the organic polymer substances. **SOLUTION:** This removing apparatus 30 comprises a pressure resistant tank 1 with a lid 2 for accommodating an object 3 to be washed, a high-pressure gas container 4, valves 5, 9, 14, and 18, a compressor 6, a solvent tank 7, high-pressure pumps 8 and 13, a heater 10, a nozzle 11, a removal acceleration constituent tank 12, a pressure adjustment valve 15, a reduced-pressure container 16, a solvent separation tank 17, and a heating gas-manufacturing apparatus 19. The object 3 to be washed is put in the pressure resistant tank 1, gas having specific pressure is filled, and fluid having specific temperature is sprayed at a pressure higher than the specific pressure.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] A fluid is used for this invention and it relates to the stripper and removing method of an organic high polymer substance which remove physically and chemically the organic high polymer substance adhered or welded, such as a work, a jig, a tool, and a device.

[0002]

[Description of the Prior Art] The method of using a fluid for the patent No. 3042076 gazette and JP, 2000-10301, A, and disassembling a high molecular compound into them as conventional technology, is indicated.

[0003] The method of performing alternative hydrolysis of nature or a synthetic high polymer is indicated without making acid or alkali exist in the patent No. 3042076 gazette substantially by using the water of a supercritical state or a subcritical state.

[0004] The method of removing resist from a washed object is indicated by the disintegration of the water of the liquid state made into high voltage by the sealed state, or a supercritical state at JP, 2000-10301, A.

[0005] The method in the conventional technology mentioned above is a method classified into a static method and a dynamic system. In this method, the resources containing the object to decompose and the washed object to which the object to decompose adhered are first put in in the resisting pressure tub which makes the decomposition reaction of a high molecular compound, etc. cause. Subsequently, it pressurizes by feeding with a pump the solvent which is a fluid which disassembles a high molecular compound, and filling a resisting pressure tub with a solvent. Subsequently, solvents formed in this way, such as a supercritical state, a subcritical state, and a liquefied gas state, decompose a high molecular compound. Although not indicated in particular in the gazette mentioned above, said washing thing is crushed finely, and also when feeding with a pump to a resisting pressure tub with a solvent, it thinks.

[0006]

[Problem(s) to be Solved by the Invention] However, there are the following problems in the above-mentioned method.

[0007] In order that, as for the first problem, these methods may fill a reactant high solvent in a resisting pressure tub, A metal impurity, organic impurities, etc. which this solvent contacted the wall of the resisting pressure tub for a long time, and elution of the metal impurity from a resisting pressure tub, organic impurities, etc. took place, and were eluted in the solvent are the point of having

an adverse effect to a washed object etc.

[0008]The second problem needs to make density of a solvent high by putting a pressure on a solvent, in order to form solvents, such as the target supercritical state, a subcritical state, and a liquefied gas state, as mentioned above.

Therefore, it is the point that must feed a solvent with high pressure pumping for a long time, and a tact time required for one processing becomes long until a solvent reaches conditions required for disassembly of a high molecular compound.

[0009]When the purpose of this invention removes an organic high polymer substance from the washed object which the organic high polymer substance adhered or welded, It is providing the stripper and removing method of an organic high polymer substance which can be done although a washed object's is not made to pollute but a tact time still more nearly required for processing is shortened with a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub with a fluid.

[0010]

[Means for Solving the Problem]A resisting pressure tub for this invention being a stripper of an organic high polymer substance which removes physically and chemically an organic high polymer substance which used a fluid, and was adhered or welded, storing said washed object, and removing said organic high polymer substance, It is a stripper of an organic high polymer substance containing a gas restoration means to fill up this resisting pressure tub with a gas of a predetermined pressure, and a hydrostatic pressure powder means to be a pressure more than said predetermined pressure, and to \*\*\*\* a fluid of a predetermined temperature at a washed object of this resisting pressure tub.

[0011]If this invention is followed, a fluid which is a solvent will be \*\*\*\*(ed) to a washed object in a resisting pressure tub, and an organic high polymer substance will be removed to it. That is, before a resisting pressure tub and a solvent contact, a fluid removes an organic high polymer substance on a washed object. Therefore, a fluid does not contact a wall of a resisting pressure tub for a long time, but there is no corrosion of a wall of a resisting pressure tub. Although a fluid is fed with high pressure pumping for a long time, it is unnecessary, until a fluid reaches conditions required for removal of an organic high polymer substance since a fluid is \*\*\*\*(ed) after pressurizing inside of a resisting pressure tub with gases other than a fluid used as a solvent by a gas restoration means a priori.

[0012]This invention is characterized by said washed object being a semiconductor wafer, a glass material, or a ceramic material.

[0013]If this invention is followed, removal of organic high polymer substances, such as resist adhering to works, such as a semiconductor wafer, a glass material, or a ceramic material, can be performed.

[0014]This invention is characterized by said fluid being a polar solvent of water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state.

[0015]Since said fluid will be a polar solvent of water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state if this invention is followed, this fluid tends to diffuse inside of a substance, and permeates a detailed portion of a washed object easily.

[0016]This invention is characterized by said gas being inactive gas. Since said gas will be inactive gas if this invention is followed, it has not said that a washed object and a chemical reaction are caused, and handling is easy.

[0017]At least one of a slit nozzle which \*\*\*\* a fluid in layers, a spraying nozzle which \*\*\*\* a fluid to misty state, and shower nozzles which \*\*\*\* a fluid in the shape of a fanning film is used for fluid rocket engine jets for this invention to \*\*\*\* a fluid in said hydrostatic pressure powder means.

[0018]Since at least one of a slit nozzle, a spraying nozzle, and shower nozzles will be used in said hydrostatic pressure powder means if this invention is followed, a fluid can be efficiently \*\*\*\*(ed) towards a washing thing and a fluid cannot scatter easily to a wall of a resisting pressure tub. A pressure of a fluid concerning a washed object by \*\*\*\* is strong.

[0019]This invention includes a removal acceleration component adding means in which said hydrostatic pressure powder means adds a removal acceleration component of said organic high polymer substance.

[0020]Since a removal acceleration component adding means which adds a removal acceleration component of said organic high polymer substance is included in said hydrostatic pressure powder means if this invention is followed, removal of an organic high polymer substance adhered or welded can be ensured in a short time.

[0021]This invention includes a washed object heating method which carries out temperature up of the washed object in a resisting pressure tub by flowing heated gas.

[0022]Since a washed object heating method which carries out temperature up of the washed object in a resisting pressure tub by flowing heated gas is included if this invention is followed, after decompressing inside of a resisting pressure tub, when taking out a washed object from a resisting pressure tub, dew condensation does not arise.

[0023]This invention includes a fluid discharge means which discharges a fluid which an organic high polymer substance removed by said hydrostatic pressure powder means mixed from a resisting pressure tub in parallel to \*\*\*\* of a fluid by said hydrostatic pressure powder means.

[0024]Since a fluid which an organic high polymer substance mixed will be discharged from a resisting pressure tub in parallel to \*\*\*\* of a fluid by said hydrostatic pressure powder means if this invention is followed, a fluid having contained an organic high polymer substance removed from a washed object does not collect in a resisting pressure tub, and this fluid does not contact a wall of a resisting pressure tub for a long time.

[0025]A pressure differential of a gas with which this invention was filled up into a resisting pressure tub by said gas restoration means, and a fluid by which twist pressure powder is carried out to said hydrostatic pressure powder means is characterized by being 490 or less kPa.

[0026]Since a pressure differential with a fluid by which twist pressure powder is carried out to a gas with which a resisting pressure tub was filled up by said gas restoration means, and said hydrostatic pressure powder means will be 490 or less kPa if this invention is followed, it is the power by \*\*\*\*, and an organic high polymer substance can be removed, without damaging a washed object.

[0027]This invention contains a means to judge a stage which removal of an organic high polymer substance adhered or welded ended to a washed object using at least one among a temperature change of the surface of a washed object, pressure variation of a fluid, and a temperature change of a fluid.

[0028]Since a stage which removal of an organic high polymer substance adhered or welded ended will be judged to a washed object using at least one among a temperature change of the surface of a washed object, pressure variation of a

fluid, and a temperature change of a fluid if this invention is followed, A stage which removal of an organic high polymer substance adhered or welded ended can be judged correctly.

[0029]A process of this invention being a removing method of an organic high polymer substance from which an organic high polymer substance which used a fluid, and was adhered or welded is removed physically and chemically, and storing said washed object to a resisting pressure tub, To a process of filling up said resisting pressure tub with a gas of a predetermined pressure, and said washed object in said resisting pressure tub, by a pressure more than said predetermined pressure. It is a removing method of an organic high polymer substance characterized by including a process of removing an organic high polymer substance adhered or welded [ said ] by \*\*\*\*(ing) a fluid of a predetermined temperature.

[0030]Since an organic high polymer substance adhered or welded [ said ] by \*\*\*\*(ing) a fluid to a washed object in a resisting pressure tub will be removed after pressurizing inside of a resisting pressure tub with a gas if this invention is followed, it is not necessary to fill a reactant high fluid in a resisting pressure tub, and this fluid does not contact a wall of a resisting pressure tub for a long time. Although a fluid is fed with high pressure pumping for a long time, it is unnecessary until a fluid reaches conditions required for removal of an organic high polymer substance.

[0031]This invention includes further a process of decompressing a pressure in said resisting pressure tub to atmospheric pressure, in order to take out said washed object from which an organic high polymer substance was removed from said resisting pressure tub.

[0032]Since a process of decompressing a pressure in said resisting pressure tub to atmospheric pressure is further included in order to take out said washed object from which an organic high polymer substance was removed from said resisting pressure tub, if this invention is followed, a washed object can be taken out safely from a resisting pressure tub.

[0033]This invention among a method of using an internal and external pressure differential of said resisting pressure tub, a method of using the difference of elevation of said resisting pressure tub and a waste fluid tub which discharges a fluid, and a method of making said resisting pressure tub incline by at least one method. A process of discharging a fluid which an organic high polymer substance removed by \*\*\*\*(ing) a fluid mixed from said resisting pressure tub is included.

[0034]By using an internal and external pressure differential of said resisting pressure tub, using the difference of elevation of said resisting pressure tub and a waste fluid tub which discharges said fluid, and making said resisting pressure tub incline, if this invention is followed. A fluid can be certainly discharged by low cost, without using a pump etc., since a fluid which an organic high polymer substance mixed is discharged from said resisting pressure tub. By discharging in this way, a fluid which an organic high polymer substance mixed does not collect in a resisting pressure tub, but it prevents this fluid contacting a wall of a resisting pressure tub for a long time.

[0035]

[Embodiment of the Invention]Drawing 1 is a schematic diagram of the stripper 30 of the organic high polymer substance which is one gestalt of operation of this invention. The stripper 30 of an organic high polymer substance is a device from which the organic high polymer substance which used the fluid, and was adhered or welded, such as a work, a jig, a tool, and a device, is removed physically and

chemically.

[0036]The stripper 30, The lid 2. Have and the washed object 3. The resisting pressure tub 1 to store, the bomb 4, the valves 5, 9, 14, and 18, the compressor 6, the solvent tank 7, the high pressure pumping 8 and 13, the heater 10, the nozzle 11, the removal acceleration component tank 12, the pressure control valve 15, the decompression container 16, the solvent liberating tank 17, And it is constituted including the heating gas manufacturing installation 19.

[0037]The resisting pressure tub 1 is a container which has the lid 2, this lid 2 is opened and the washed object 3 is stored in the resisting pressure tub 3.

[0038]The gas for making the inside of the resisting pressure tub 1 into a predetermined pressure is stored in the bomb 4. The compressor 6 for carrying out pressure up of said gas is connected to this bomb 4, and this compressor 6 is connected to the resisting pressure tub 1 via the valve 5.

[0039]The fluid for removing the organic high polymer substance adhered or welded 3 is contained in the solvent tank 7. The high pressure pumping 8 for carrying out pressure up of said fluid is connected to this solvent tank 7, and this high pressure pumping 8 is connected to the heater 10 for carrying out temperature up of said fluid to a predetermined temperature via the valve 9. Said heater 10 is connected to the nozzle 11. This nozzle 11 is formed in the inside of the resisting pressure tub 1, and \*\*\*\* a fluid towards the washed object which the organic high polymer substance adhered or welded.

[0040]The ingredient which promotes removal of an organic high polymer substance is contained in the removal acceleration component tank 12. The high pressure pumping 13 for carrying out pressure up of said removal acceleration component is connected to this removal acceleration component tank 12, and the valve 14 is connected to this high pressure pumping 13. The valve 14 is connected to the exit of the heater 10 so that the removal acceleration component which passed this valve 14 may be mixed with said fluid heated with said heater 10.

[0041]The pressure control valve 15 is formed in the outside of the resisting pressure tub 1, adjusts the pressure in the resisting pressure tub 1 by opening and closing this pressure control valve 15, or discharges the fluid which collects in the resisting pressure tub 1 besides the resisting pressure tub 1. The decompression container 16 for collecting the fluids which the removed organic high polymer substance mixed is connected to this pressure control valve 15. The solvent liberating tank 17 which collects the supernatant liquid in which the organic high polymer substance removed from the fluid was separated is connected to this decompression container 16.

[0042]The heating gas manufacturing installation 19 is connected to the resisting pressure tub 1 via the valve 18. In this heating gas manufacturing installation 19, gas is heated, heating gas is sprayed on the washed object 3 which removal of the organic high polymer substance ended through the valve 18, and temperature up of the washed object 3 is carried out.

[0043]Drawing 2 is process drawing showing the removing method of the organic high polymer substance which are other gestalten of operation of this invention. The removing method of the organic high polymer substance of this invention used for below with the resist removing device of a liquid crystal panel manufacturing installation with reference to drawing 1 and drawing 2 is explained. In detail, when novolac type photoresist is applied on the glass substrate of a liquid crystal panel, how to remove this resist is explained.

[0044]First, the lid 2 is opened in order to put the glass substrate of the liquid

crystal panel which is the washed object 3 into the resisting pressure tub 1 (drawing 2 (a)). The glass substrate in which the resist which is an organic high polymer substance for removal has adhered to the surface is stored in the resisting pressure tub 1 (drawing 2 (b)), and the lid 2 is shut (drawing 2 (c)). Two or more sheets are arranged in the resisting pressure tub 1, glass substrates keep a certain amount of interval, and a glass substrate is put in order so that the field where resist is applied may become vertical to the bottom of the resisting pressure tub 1.

[0045]Next, the valve 5 is opened wide and the carbon dioxide which is a gas is poured into the resisting pressure tub 1 from the bomb 4. The compressor 6 is operated and pressure up is carried out until the pressure in the resisting pressure tub 1 reaches 5MPa. The valve 5 will be closed if the pressure in the resisting pressure tub 1 is set to 5MPa with carbon dioxide (drawing 2 (d)).

[0046]Next, operation of the high pressure pumping 8 is started (drawing 2 (e)), and the water which is a fluid is sent out to the high pressure pumping 8 from the solvent tank 7 by opening the valve 9. A pressure heats the water used as 5.1MPa to through and 200 °C to the heater 10 by going via the high pressure pumping 8.

[0047]An ammonia solution is mixed in 5.1MPa and the water used as 200 °C, i.e., the water of a subcritical state, as a removal acceleration component. The ammonia solution stored in the removal acceleration component tank 12 is mixed by the water which pressure up was carried out with the high pressure pumping 13, and was heated with the heater 10 through the valve 14 (drawing 2 (f-2)). The water of a subcritical state with which the ammonia solution was mixed is mixed towards a glass substrate through the nozzle 11 (drawing 2 (f-1)).

[0048]Although the removing time of the resist when completely not mixing an ammonia solution is 10 minutes, when an ammonia solution is mixed so that it may become water of a subcritical state with 10 ppm, it is 5 minutes, and the removing time of resist can be shortened.

[0049]As said removal acceleration component, fluoric acid solution, a hydrochloric acid aqueous solution, a nitric acid solution, phosphoric acid solution, hydrogen peroxide solution, etc. besides an ammonia solution may be used. Although the water of the subcritical state is used as a fluid which mixed to a glass substrate, the water of a supercritical state may be sufficient. It is not necessary to make the water of a subcritical state mix said removal acceleration component depending on the case.

[0050]Here, the state where the both sides of the critical pressure peculiar to a substance and critical temperature were exceeded is pointed out, and, as for a supercritical state, a subcritical state refers to the state where 1/5 of the critical pressure peculiar to a substance and one fifth of the both sides of critical temperature were exceeded. The critical pressure of water is 22.1MPa and critical temperature is 374 °C.

[0051]Compared with a gas, density is large, since the fluid of a subcritical state thru/or a supercritical state has small viscosity compared with a fluid, it permeates the detailed portion of a glass substrate easily, and its reactivity is also high. Therefore, the resist on a glass substrate is cheaply removable by using the water of a subcritical state as a fluid.

[0052]The water of the subcritical state which filled up the resisting pressure tub 1 with carbon dioxide, and mixed the ammonia solution by mixed to a glass substrate so that it may mention above. While resist is physically removable with a high pressure, resist is chemically removable by the dissolution or decomposition

by water of said subcritical state (drawing 2 (g)).

[0053] Since it is \*\*\*\*(ed) to the resisting pressure tub 1 like conventional technology rather than filling the water of a subcritical state, the water of a reactant high subcritical state does not contact the wall of the resisting pressure tub 1 for a long time, and a glass substrate is not polluted with a metal impurity, organic impurities, etc. which are eluted from the resisting pressure tub 1.

[0054] In conventional technology, a fluid is made into the elevated temperature and high voltage from which a fluid will be in a subcritical state thru/or a supercritical state with the high pressure pumping 8 and the heater 10, and it is necessary to feed to the resisting pressure tub 1 until a fluid reaches conditions required for removal of an organic high polymer substance. However, since there is a limit in the liquid-sending capability of the high pressure pumping 8, a long time is required for filling a hot and high-pressure fluid to the resisting pressure tub 1. Therefore, to raise the pressure of a fluid for a short time, it is necessary to enlarge capability of the high pressure pumping 8 and the heater 10.

[0055] On the other hand, a hot and high-pressure fluid is not filled with this invention in large quantities to the resisting pressure tub 1, but a fluid is \*\*\*\*(ed), and it applies to a washed object. That is, since an organic high polymer substance is removed by carrying out every pressure powder of a little fluids [ some of ] of an elevated temperature and high voltage to the resisting pressure tub 1 with which the gas of the predetermined pressure was filled up beforehand, it is not necessary to make a lot of fluids into an elevated temperature and high voltage, and to feed them at once. Therefore, it is not necessary to enlarge capability of the high pressure pumping 8 and the heater 10, time to start the pressure buildup of a fluid can be shortened, and a tact time required for processing can be shortened.

[0056] If the processing time of the conventional removing method at the time of actually using the pump of the same liquid-sending capability and the removing method in this invention is compared, it is about about 10 times as many differences, and according to the removing method in this invention, processing time can be shortened substantially.

[0057] As the nozzle 11, the slit nozzle which \*\*\*\* a fluid in layers is used. Two or more these slit nozzles are arranged so that it may become parallel to a glass substrate, for example. Since the slit nozzle can \*\*\*\* a fluid in layers, cannot scatter easily around and does not require the water of a subcritical state for the wall of the resisting pressure tub 1 easily when the water of a subcritical state is \*\*\*\*(ed) to a glass substrate, its effect of preventing the corrosion of the resisting pressure tub 1 is high.

[0058] As the nozzle 11, the spraying nozzle which \*\*\*\* a fluid to misty state, the shower nozzle which \*\*\*\* a fluid in the shape of [ of a single flat surface ] a sector film, etc. may be used. These nozzles have a high effect which reduces the amount of \*\*\*\* of a fluid. The effect of a shower nozzle of physical removal of the resist by the high voltage shower washing using the \*\*\*\* pressure of the fluid is high. The nozzle mentioned above may be used independently and may be used together.

[0059] The difference of the pressure of the water \*\*\*\*(ed) from the nozzle 11 and the pressure in the resisting pressure tub 1 is below 490kPa (5kgf/cm<sup>2</sup>) preferably. If setting a pressure differential to 490 or less kPa has a pressure differential larger than 490kPa, when removing the resist on the glass substrate which breaks easily, it is because it becomes easy to damage a glass substrate with a \*\*\*\*



pressure.

[0060]Next, the pressure control valve 15 is passed, and the water of the subcritical state having contained the removed resist is discharged from the resisting pressure tub 1, and is collected to the decompression container 16 (drawing 2 (h)). Discharge from the resisting pressure tub 1 of the water of this subcritical state is performed in parallel to \*\*\*\* of the water of the subcritical state to a glass substrate.

[0061]As a method of promoting the discharge to the decompression container 16, a pressure differential or the difference of elevation is provided between the resisting pressure tub 1 and the decompression container 16, and the method of using them and the method of making the resisting pressure tub 1 incline are mentioned. This method may be used independently and may be used together.

[0062]In order that the carbon dioxide in the resisting pressure tub 1 may fall out from the pressure control valve 15 continuously at this time, the pressure in the resisting pressure tub 1 is maintained at 5MPa by opening the valve 5 wide and sometimes sending carbon dioxide into the resisting pressure tub 1.

[0063]Since the fluid in which reactivity increased is filled with conventional technology to the resisting pressure tub 1 as stated even in the top, the metallic material of the wall of the resisting pressure tub 1 may be melted, and the washed object 3 may be polluted with the eluted metallic material. The contamination by the metal in which especially the washed object 3 is eluted in the case of the glass substrate of a semiconductor and a liquid crystal panel, etc. gives a fatal damage to the yield of a product. For example, even when SUS316L which is a charge of a stainless steel material is used as a material of the resisting pressure tub 1 and a stable oxide film is formed in the surface, the surface is corroded at about 0.1 mm/day in speed. The metal which was corroded and was eluted adheres to a glass substrate, and stops accomplishing the business as a glass substrate of a liquid crystal panel. In this invention, this problem is solved, and since the water of a subcritical state is not made to stagnate in the resisting pressure tub 1 for a long time but is discharged promptly, said contamination does not take place.

[0064]Since the water collected by the decompression container 16 separates from the temperature and the pressure conditions which were given by the resisting pressure tub 1, the removal performance of resist is lost quickly and the organic substance removed in the decompression container 16 deposits. When a fluid is water of a subcritical state, the decomposition reaction of resist occurs preferentially and a with a molecular weight [ with benzene skeletons ] of about 100 to 200 organic substance deposits.

[0065]The supernatant water in the decompression container 16 is discharged to the solvent liberating tank 17 using the difference of elevation or a pump, and is again used as a fluid of resist removal through waste water treatment equipments (not shown), such as activated carbon, ion-exchange resin, bio-processing, UV disinfection, and a semipermeable membrane, a water purifying apparatus (not shown), etc.

[0066]Since heat occurs by the decomposition reaction of resist in spite of \*\*\*\* (ing) the water of the subcritical state which are 5.1MPa and 200 \*\* to the glass substrate, the resist surface temperature on a glass substrate amounts to 220 \*\*. This is used and the end time of a removal reaction is judged by measuring the temperature change on the surface of a glass substrate, the temperature change of the water of a subcritical state which finished reacting, etc. The end time of this removal reaction may be judged by measuring the pressure variation of the water of

a subcritical state. That is, while the removal reaction is progressing continuously, the pressure in the resisting pressure layer 1 continues rising. If a removal reaction approaches an end, the increasing rate of the pressure in the resisting pressure layer 1 decreases. As mentioned above, in order to make regularity the pressure in the resisting pressure layer 1 which decreases by discharging the water of a subcritical state from the resisting pressure layer 1, the valve 5 is opened wide, carbon dioxide is sent into the resisting pressure layer 1, and the pressure in the resisting pressure layer 1 is maintained at 5MPa. Therefore, in the interval from opening of this valve 5 to opening of the following valve 5, compared with the early stages of a reaction, the direction of the telophase of a reaction becomes narrow. The end time of a removal reaction is judged using this.

[0067]Next, after the water of the subcritical state \*\*\*\*(ed) from the nozzle 11 finishes removing resist from a glass substrate, it closes the valve 9 and the valve 14, stops \*\*\*\* of the water of a subcritical state (drawing 2 (i)), and suspends a resist removal reaction (drawing 2 (j)).

[0068]Next, after fully discharging the water of a subcritical state from the resisting pressure tub 1, the opening of the pressure control valve 15 is changed and the pressure of the resisting pressure tub 1 is decompressed even to atmospheric pressure (drawing 2 (k)). A glass substrate is quenched by the adiabatic expansion by reducing the pressure in the resisting pressure tub 1 rapidly. It may dew, if the lid 2 is opened and a glass substrate is taken out as it is. In order to prevent this, the heating nitrogen made by the heating gas manufacturing installation 19 is injected to a glass substrate through the valve 18 (drawing 2 (l)).

[0069]In order to inject heating gas uniformly at this time, a nozzle may be provided inside the resisting pressure tub 1, and it may connect with the valve 18. By using this nozzle, the amount of the nitrogen used is made in half. In the embodiment of this invention, although heating nitrogen was used, other gas may be used.

[0070]With heating nitrogen, if a glass substrate is warmed more than the dew point, the lid 2 will be opened and a glass substrate will be taken out (drawing 2 (m)).

[0071]Although an expensive solvent and ozone must be used for resist removing and expenses, such as flue gas treatment, solvent purchase, and solvent treatment, are needed for it in the former, Since cheap water is used as a fluid and special processing is not needed, either, when the removing method of the organic high polymer substance of this invention is used with the resist removing device of a liquid crystal panel manufacturing installation as mentioned above, with this device, resist removing can be performed cheaply.

[0072]Although the embodiment mentioned above explained the case where the removing method of the organic high polymer substance of this invention was used with the resist removing device of a liquid crystal panel manufacturing installation, it may use with the resist removing device in a semiconductor substrate manufacturing installation, a solar cell manufacturing installation, an opto device manufacturing installation, etc.

[0073]Although the case where the resist applied to the glass substrate which is the washed object 3 was removed was described, even if the washed objects 3 are works (a semiconductor wafer, a glass material, a ceramic material, etc.) other than a glass substrate, a jig, a tool, a device, etc., they can apply this

invention.

[0074]As resist for removal, even when removing not only novolac type photoresist but negative-mold novolak resin resist, positive type rubber system resist, etc., the same result is obtained. Reaction time changes with the coating weight of resist, curing conditions, impurity quantity, leaving times, organic components, etc.

[0075]As a candidate for removal, even if it is dioxin, PBC, activated sludge, and other organic high polymer substances, this invention is applicable.

[0076]As a fluid, the polar solvent of not only water but a subcritical state thru/or a supercritical state may be used. A pressure and temperature are higher than atmospheric pressure and a room temperature, and as long as the density is a fluid which is more than  $0.1 \text{ g/cm}^3$ , it may use as a fluid in this invention.

[0077]The same result is obtained, even if the polar solvent which dissolves in water, such as methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, acetic acid, phenol, and DMSO (dimethyl sulfoxide), is mentioned and it uses these as said polar solvent. Unlike the case where water is used, at this time, processing time, temperature, a pressure, etc. serve as conditions peculiar to each polar solvent. The case where a decomposition reaction occurs preferentially depending on the kind of polar solvent to be used, and lytic reaction may occur preferentially. For example, when DMSO is used for a fluid, lytic reaction occurs preferentially.

[0078]Although the carbon dioxide which is inactive gas was used in the embodiment mentioned above as a gas with which the resisting pressure tub 1 is filled up, other inactive gas may be used.

[0079]

[Effect of the Invention]As mentioned above, according to this invention, since it is not necessary to fill a reactant high fluid in a resisting pressure tub and this fluid does not contact the wall of a resisting pressure tub for a long time, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented. Since it is unnecessary although a fluid is fed with high pressure pumping for a long time until a fluid reaches conditions required for removal of an organic high polymer substance, time to start the pressure buildup of a solvent can be shortened and a tact time required for processing can be shortened.

[0080]According to this invention, removal of organic high polymer substances, such as resist adhering to works, such as a semiconductor wafer, a glass material, or a ceramic material, can be performed.

[0081]Since said fluid is a polar solvent of the water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state according to this invention, this fluid tends to diffuse the inside of a substance, and permeates the detailed portion of a washed object easily. Therefore, an organic high polymer substance can be removed more certainly in a short time. Since water and a polar solvent are cheap, the removal cost of an organic high polymer substance can be held down.

[0082]According to this invention, since said gas is inactive gas, it has not said that a washed object and a chemical reaction are caused, and is easy also for handling. Since inactive gas is cheap, the removal cost of an organic high polymer substance can be held down.

[0083]Since said nozzle is used according to this invention, it can \*\*\*\* efficiently towards a washed object and a fluid cannot scatter easily to the wall

of a resisting pressure tub. Therefore, since this fluid does not contact the wall of a resisting pressure tub for a long time, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented. Since the pressure of the fluid concerning the washed object by \*\*\*\* is strong, an organic high polymer substance can be removed more certainly.

[0084]According to this invention, since the removal acceleration component which carries out promotion of removal of an organic high polymer substance to a fluid is added, removal of the organic high polymer substance adhered or welded can be ensured in a short time. Therefore, the removing time of an organic high polymer substance can be shortened.

[0085]According to this invention, since temperature up of the washed object is carried out by the heated gas before taking out a washed object from a resisting pressure tub, after decompressing the inside of a resisting pressure tub, the dew condensation produced when taking out a washed object from a resisting pressure tub can be prevented.

[0086]According to this invention, since the fluid which the removed organic high polymer substance mixed is discharged from a resisting pressure tub in parallel to \*\*\*\* of a fluid, the fluid having contained the organic high polymer substance removed from the washed object does not collect in a resisting pressure tub, and this fluid does not contact the wall of a resisting pressure tub for a long time. Therefore, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented.

[0087]According to this invention, since the pressure differential with the fluid by which twist pressure powder is carried out to the gas with which the resisting pressure tub was filled up by said gas restoration means, and said hydrostatic pressure powder means is 490 or less kPa, it can remove an organic high polymer substance, without damaging a washed object by the power by \*\*\*\*.

[0088]Since the stage which removal of the organic high polymer substance adhered or welded ended is judged to a washed object using at least one among the temperature change of the surface of a washed object, the pressure variation of a fluid, and the temperature change of a fluid according to this invention, The stage which removal of the organic high polymer substance adhered or welded ended can be judged correctly. Therefore, removal of an organic high polymer substance can be ensured.

[0089]According to this invention, by the process of \*\*\*\*(ing) a fluid to the washed object in a resisting pressure tub, since the organic high polymer substance adhered or welded [ said ] is removed, it is not necessary to fill a reactant high fluid in a resisting pressure tub, and this fluid does not contact the wall of a resisting pressure tub for a long time. Therefore, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented. Although a fluid is fed with high pressure pumping for a long time, it is unnecessary until a fluid reaches conditions required for removal of an organic high polymer substance. Therefore, time to start the pressure buildup of a solvent can be shortened and a tact time required for processing can be shortened.

[0090]According to this invention, since the pressure in said resisting pressure tub is decompressed to atmospheric pressure in order to take out said washed object from which the organic high polymer substance was removed from said resisting pressure tub, a washed object can be taken out safely from a resisting pressure

tub.

[0091]According to this invention, since the fluid which the organic high polymer substance removed by \*\*\*\*(ing) a fluid mixed is discharged from said resisting pressure tub, the fluid which the organic high polymer substance removed in the resisting pressure tub mixed does not collect in this resisting pressure tub, and this fluid does not contact the wall of a resisting pressure tub for a long time. Therefore, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented.

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CLAIMS

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[Claim(s)]

[Claim 1] A stripper of an organic high polymer substance characterized by comprising the following which removes physically and chemically an organic high polymer substance which used a fluid, and was adhered or welded.

A resisting pressure tub for storing said washed object and removing said organic high polymer substance.

A gas restoration means to fill up this resisting pressure tub with a gas of a predetermined pressure.

A hydrostatic pressure powder means to \*\*\*\* a fluid of a predetermined temperature by a pressure more than said predetermined pressure to a washed object of this resisting pressure tub.

[Claim 2] A stripper of the organic high polymer substance according to claim 1, wherein said washed object is a semiconductor wafer, a glass material, or a ceramic material.

[Claim 3] A stripper of the organic high polymer substance according to claim 1, wherein said fluid is a polar solvent of water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state.

[Claim 4] A stripper of the organic high polymer substance according to claim 1, wherein said gas is inactive gas.

[Claim 5] In said hydrostatic pressure powder means, fluid rocket engine jets for \*\*\*\*(ing) a fluid, A stripper of the organic high polymer substance according to any one of claims 1 to 4 using at least one of a slit nozzle which \*\*\*\* a fluid in layers, a spraying nozzle which \*\*\*\* a fluid to misty state, and shower nozzles which \*\*\*\* a fluid in the shape of a fanning film.

[Claim 6] A stripper of the organic high polymer substance according to any one of claims 1 to 5, wherein said hydrostatic pressure powder means includes a removal acceleration component adding means which adds a removal acceleration component of said organic high polymer substance.

[Claim 7] A stripper of the organic high polymer substance according to claim 1 including a washed object heating method which carries out temperature up of the washed object in a resisting pressure tub by flowing heated gas.

[Claim 8] A stripper of the organic high polymer substance according to claim 1 including a fluid discharge means which discharges a fluid which an organic high polymer substance removed by said hydrostatic pressure powder means mixed from a resisting pressure tub in parallel to \*\*\*\* of a fluid by said hydrostatic pressure powder means.

[Claim 9]A stripper of the organic high polymer substance according to claim 1, wherein a pressure differential of a gas with which a resisting pressure tub was filled up by said gas restoration means, and a fluid by which twist pressure powder is carried out to said hydrostatic pressure powder means is 490 or less kPa.

[Claim 10]A stage which removal of an organic high polymer substance adhered or welded ended, A stripper of the organic high polymer substance according to any one of claims 1 to 9 containing a means to judge using at least one among a temperature change of the surface of a washed object, pressure variation of a fluid, and a temperature change of a fluid.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is a schematic diagram of the stripper 30 of the organic high polymer substance which is one gestalt of operation of this invention.

[Drawing 2] It is process drawing showing the removing method of the organic high polymer substance which are other gestalten of operation of this invention.

[Description of Notations]

- 1 Resisting pressure tub
- 2 Lid
- 3 Washed object
- 4 Bomb
- 5, 9, 14, and 18 Valve
- 6 Compressor
- 7 Solvent tank
- 8, 13 high pressure pumping
- 10 Heater
- 11 Nozzle
- 12 Removal acceleration component tank
- 15 Pressure control valve
- 16 Decompression container
- 17 Solvent liberating tank
- 19 Heating gas manufacturing installation

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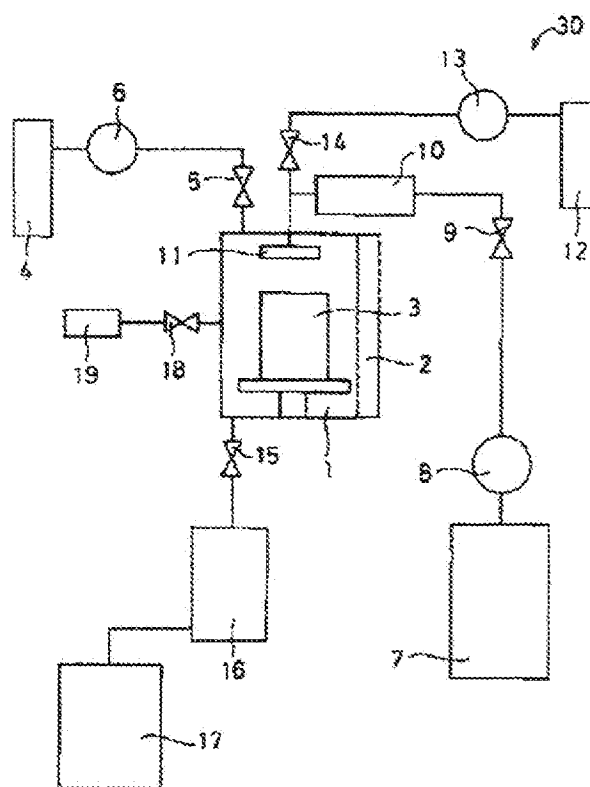
# APPARATUS AND METHOD FOR REMOVING ORGANIC POLYMER SUBSTANCE

Patent number: JP2002343760  
 Publication date: 2002-11-29  
 Inventor: ONO HITOSHI  
 Applicant: SHARP KK  
 Classification:  
 - international: H01L21/304; B08B3/08; B08B5/00; B08B7/00;  
 H01L21/027; H01L21/306; H01L21/3065  
 - european:  
 Application number: JP20010151127 20010521  
 Priority number(s): JP20010151127 20010521

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## Abstract of JP2002343760

**PROBLEM TO BE SOLVED:** To provide the removing apparatus of organic polymer substances that can reduce fact time required for treatment without contaminating an object to be washed with metal and organic impurities or the like being eluted from a pressure resistant tank by fluid, when the organic polymer substances are removed from the object to be washed where the organic polymer substance adheres or welds, and to provide the removing method of the organic polymer substances. **SOLUTION:** This removing apparatus 30 comprises a pressure resistant tank 1 with a lid 2 for accommodating an object 3 to be washed, a high-pressure gas container 4, valves 5, 9, 14, and 18, a compressor 6, a solvent tank 7, high-pressure pumps 8 and 13, a heater 10, a nozzle 11, a removal acceleration constituent tank 12, a pressure adjustment valve 15, a reduced-pressure container 16, a solvent separation tank 17, and a heating gas-manufacturing apparatus 19. The object 3 to be washed is put in the pressure resistant tank 1, gas having specific pressure is filled, and fluid having specific temperature is sprayed at a pressure higher than the specific pressure.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] A fluid is used for this invention and it relates to the stripper and removing method of an organic high polymer substance which remove physically and chemically the organic high polymer substance adhered or welded, such as a work, a jig, a tool, and a device.

[0002]

[Description of the Prior Art] The method of using a fluid for the patent No. 3042076 gazette and JP, 2000-10301, A, and disassembling a high molecular compound into them as conventional technology, is indicated.

[0003] The method of performing alternative hydrolysis of nature or a synthetic high polymer is indicated without making acid or alkali exist in the patent No. 3042076 gazette substantially by using the water of a supercritical state or a subcritical state.

[0004] The method of removing resist from a washed object is indicated by the disintegration of the water of the liquid state made into high voltage by the sealed state, or a supercritical state at JP, 2000-10301, A.

[0005] The method in the conventional technology mentioned above is a method classified into a static method and a dynamic system. In this method, the resources containing the object to decompose and the washed object to which the object to decompose adhered are first put in in the resisting pressure tub which makes the decomposition reaction of a high molecular compound, etc. cause. Subsequently, it pressurizes by feeding with a pump the solvent which is a fluid which disassembles a high molecular compound, and filling a resisting pressure tub with a solvent. Subsequently, solvents formed in this way, such as a supercritical state, a subcritical state, and a liquefied gas state, decompose a high molecular compound. Although not indicated in particular in the gazette mentioned above, said washing thing is crushed finely, and also when feeding with a pump to a resisting pressure tub with a solvent, it thinks.

[0006]

[Problem(s) to be Solved by the Invention] However, there are the following problems in the above-mentioned method.

[0007] In order that, as for the first problem, these methods may fill a reactant high solvent in a resisting pressure tub, A metal impurity, organic impurities, etc. which this solvent contacted the wall of the resisting pressure tub for a long time, and elution of the metal impurity from a resisting pressure tub, organic impurities, etc. took place, and were eluted in the solvent are the point of having

an adverse effect to a washed object etc.

[0008]The second problem needs to make density of a solvent high by putting a pressure on a solvent, in order to form solvents, such as the target supercritical state, a subcritical state, and a liquefied gas state, as mentioned above.

Therefore, it is the point that must feed a solvent with high pressure pumping for a long time, and a tact time required for one processing becomes long until a solvent reaches conditions required for disassembly of a high molecular compound.

[0009]When the purpose of this invention removes an organic high polymer substance from the washed object which the organic high polymer substance adhered or welded, It is providing the stripper and removing method of an organic high polymer substance which can be done although a washed object's is not made to pollute but a tact time still more nearly required for processing is shortened with a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub with a fluid.

[0010]

[Means for Solving the Problem]A resisting pressure tub for this invention being a stripper of an organic high polymer substance which removes physically and chemically an organic high polymer substance which used a fluid, and was adhered or welded, storing said washed object, and removing said organic high polymer substance, It is a stripper of an organic high polymer substance containing a gas restoration means to fill up this resisting pressure tub with a gas of a predetermined pressure, and a hydrostatic pressure powder means to be a pressure more than said predetermined pressure, and to \*\*\*\* a fluid of a predetermined temperature at a washed object of this resisting pressure tub.

[0011]If this invention is followed, a fluid which is a solvent will be \*\*\*\*(ed) to a washed object in a resisting pressure tub, and an organic high polymer substance will be removed to it. That is, before a resisting pressure tub and a solvent contact, a fluid removes an organic high polymer substance on a washed object. Therefore, a fluid does not contact a wall of a resisting pressure tub for a long time, but there is no corrosion of a wall of a resisting pressure tub. Although a fluid is fed with high pressure pumping for a long time, it is unnecessary, until a fluid reaches conditions required for removal of an organic high polymer substance since a fluid is \*\*\*\*(ed) after pressurizing inside of a resisting pressure tub with gases other than a fluid used as a solvent by a gas restoration means a priori.

[0012]This invention is characterized by said washed object being a semiconductor wafer, a glass material, or a ceramic material.

[0013]If this invention is followed, removal of organic high polymer substances, such as resist adhering to works, such as a semiconductor wafer, a glass material, or a ceramic material, can be performed.

[0014]This invention is characterized by said fluid being a polar solvent of water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state.

[0015]Since said fluid will be a polar solvent of water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state if this invention is followed, this fluid tends to diffuse inside of a substance, and permeates a detailed portion of a washed object easily.

[0016]This invention is characterized by said gas being inactive gas. Since said gas will be inactive gas if this invention is followed, it has not said that a washed object and a chemical reaction are caused, and handling is easy.

[0017]At least one of a slit nozzle which \*\*\*\* a fluid in layers, a spraying nozzle which \*\*\*\* a fluid to misty state, and shower nozzles which \*\*\*\* a fluid in the shape of a fanning film is used for fluid rocket engine jets for this invention to \*\*\*\* a fluid in said hydrostatic pressure powder means.

[0018]Since at least one of a slit nozzle, a spraying nozzle, and shower nozzles will be used in said hydrostatic pressure powder means if this invention is followed, a fluid can be efficiently \*\*\*\*(ed) towards a washing thing and a fluid cannot scatter easily to a wall of a resisting pressure tub. A pressure of a fluid concerning a washed object by \*\*\*\* is strong.

[0019]This invention includes a removal acceleration component adding means in which said hydrostatic pressure powder means adds a removal acceleration component of said organic high polymer substance.

[0020]Since a removal acceleration component adding means which adds a removal acceleration component of said organic high polymer substance is included in said hydrostatic pressure powder means if this invention is followed, removal of an organic high polymer substance adhered or welded can be ensured in a short time.

[0021]This invention includes a washed object heating method which carries out temperature up of the washed object in a resisting pressure tub by flowing heated gas.

[0022]Since a washed object heating method which carries out temperature up of the washed object in a resisting pressure tub by flowing heated gas is included if this invention is followed, after decompressing inside of a resisting pressure tub, when taking out a washed object from a resisting pressure tub, dew condensation does not arise.

[0023]This invention includes a fluid discharge means which discharges a fluid which an organic high polymer substance removed by said hydrostatic pressure powder means mixed from a resisting pressure tub in parallel to \*\*\*\* of a fluid by said hydrostatic pressure powder means.

[0024]Since a fluid which an organic high polymer substance mixed will be discharged from a resisting pressure tub in parallel to \*\*\*\* of a fluid by said hydrostatic pressure powder means if this invention is followed, a fluid having contained an organic high polymer substance removed from a washed object does not collect in a resisting pressure tub, and this fluid does not contact a wall of a resisting pressure tub for a long time.

[0025]A pressure differential of a gas with which this invention was filled up into a resisting pressure tub by said gas restoration means, and a fluid by which twist pressure powder is carried out to said hydrostatic pressure powder means is characterized by being 490 or less kPa.

[0026]Since a pressure differential with a fluid by which twist pressure powder is carried out to a gas with which a resisting pressure tub was filled up by said gas restoration means, and said hydrostatic pressure powder means will be 490 or less kPa if this invention is followed, it is the power by \*\*\*\*, and an organic high polymer substance can be removed, without damaging a washed object.

[0027]This invention contains a means to judge a stage which removal of an organic high polymer substance adhered or welded ended to a washed object using at least one among a temperature change of the surface of a washed object, pressure variation of a fluid, and a temperature change of a fluid.

[0028]Since a stage which removal of an organic high polymer substance adhered or welded ended will be judged to a washed object using at least one among a temperature change of the surface of a washed object, pressure variation of a

fluid, and a temperature change of a fluid if this invention is followed. A stage which removal of an organic high polymer substance adhered or welded ended can be judged correctly.

[0029]A process of this invention being a removing method of an organic high polymer substance from which an organic high polymer substance which used a fluid, and was adhered or welded is removed physically and chemically, and storing said washed object to a resisting pressure tub, To a process of filling up said resisting pressure tub with a gas of a predetermined pressure, and said washed object in said resisting pressure tub, by a pressure more than said predetermined pressure. It is a removing method of an organic high polymer substance characterized by including a process of removing an organic high polymer substance adhered or welded [ said ] by \*\*\*\*(ing) a fluid of a predetermined temperature.

[0030]Since an organic high polymer substance adhered or welded [ said ] by \*\*\*\*(ing) a fluid to a washed object in a resisting pressure tub will be removed after pressurizing inside of a resisting pressure tub with a gas if this invention is followed, it is not necessary to fill a reactant high fluid in a resisting pressure tub, and this fluid does not contact a wall of a resisting pressure tub for a long time. Although a fluid is fed with high pressure pumping for a long time, it is unnecessary until a fluid reaches conditions required for removal of an organic high polymer substance.

[0031]This invention includes further a process of decompressing a pressure in said resisting pressure tub to atmospheric pressure, in order to take out said washed object from which an organic high polymer substance was removed from said resisting pressure tub.

[0032]Since a process of decompressing a pressure in said resisting pressure tub to atmospheric pressure is further included in order to take out said washed object from which an organic high polymer substance was removed from said resisting pressure tub, if this invention is followed, a washed object can be taken out safely from a resisting pressure tub.

[0033]This invention among a method of using an internal and external pressure differential of said resisting pressure tub, a method of using the difference of elevation of said resisting pressure tub and a waste fluid tub which discharges a fluid, and a method of making said resisting pressure tub incline by at least one method. A process of discharging a fluid which an organic high polymer substance removed by \*\*\*\*(ing) a fluid mixed from said resisting pressure tub is included.

[0034]By using an internal and external pressure differential of said resisting pressure tub, using the difference of elevation of said resisting pressure tub and a waste fluid tub which discharges said fluid, and making said resisting pressure tub incline, if this invention is followed. A fluid can be certainly discharged by low cost, without using a pump etc., since a fluid which an organic high polymer substance mixed is discharged from said resisting pressure tub. By discharging in this way, a fluid which an organic high polymer substance mixed does not collect in a resisting pressure tub, but it prevents this fluid contacting a wall of a resisting pressure tub for a long time.

[0035]

[Embodiment of the Invention]Drawing 1 is a schematic diagram of the stripper 30 of the organic high polymer substance which is one gestalt of operation of this invention. The stripper 30 of an organic high polymer substance is a device from which the organic high polymer substance which used the fluid, and was adhered or welded, such as a work, a jig, a tool, and a device, is removed physically and

chemically.

[0036]The stripper 30, The lid 2. Have and the washed object 3. The resisting pressure tub 1 to store, the bomb 4, the valves 5, 9, 14, and 18, the compressor 6, the solvent tank 7, the high pressure pumping 8 and 13, the heater 10, the nozzle 11, the removal acceleration component tank 12, the pressure control valve 15, the decompression container 16, the solvent liberating tank 17, And it is constituted including the heating gas manufacturing installation 19.

[0037]The resisting pressure tub 1 is a container which has the lid 2, this lid 2 is opened and the washed object 3 is stored in the resisting pressure tub 3.

[0038]The gas for making the inside of the resisting pressure tub 1 into a predetermined pressure is stored in the bomb 4. The compressor 6 for carrying out pressure up of said gas is connected to this bomb 4, and this compressor 6 is connected to the resisting pressure tub 1 via the valve 5.

[0039]The fluid for removing the organic high polymer substance adhered or welded 3 is contained in the solvent tank 7. The high pressure pumping 8 for carrying out pressure up of said fluid is connected to this solvent tank 7, and this high pressure pumping 8 is connected to the heater 10 for carrying out temperature up of said fluid to a predetermined temperature via the valve 9. Said heater 10 is connected to the nozzle 11. This nozzle 11 is formed in the inside of the resisting pressure tub 1, and \*\*\*\* a fluid towards the washed object which the organic high polymer substance adhered or welded.

[0040]The ingredient which promotes removal of an organic high polymer substance is contained in the removal acceleration component tank 12. The high pressure pumping 13 for carrying out pressure up of said removal acceleration component is connected to this removal acceleration component tank 12, and the valve 14 is connected to this high pressure pumping 13. The valve 14 is connected to the exit of the heater 10 so that the removal acceleration component which passed this valve 14 may be mixed with said fluid heated with said heater 10.

[0041]The pressure control valve 15 is formed in the outside of the resisting pressure tub 1, adjusts the pressure in the resisting pressure tub 1 by opening and closing this pressure control valve 15, or discharges the fluid which collects in the resisting pressure tub 1 besides the resisting pressure tub 1. The decompression container 16 for collecting the fluids which the removed organic high polymer substance mixed is connected to this pressure control valve 15. The solvent liberating tank 17 which collects the supernatant liquid in which the organic high polymer substance removed from the fluid was separated is connected to this decompression container 16.

[0042]The heating gas manufacturing installation 19 is connected to the resisting pressure tub 1 via the valve 18. In this heating gas manufacturing installation 19, gas is heated, heating gas is sprayed on the washed object 3 which removal of the organic high polymer substance ended through the valve 18, and temperature up of the washed object 3 is carried out.

[0043]Drawing 2 is process drawing showing the removing method of the organic high polymer substance which are other gestalten of operation of this invention. The removing method of the organic high polymer substance of this invention used for below with the resist removing device of a liquid crystal panel manufacturing installation with reference to drawing 1 and drawing 2 is explained. In detail, when novolac type photoresist is applied on the glass substrate of a liquid crystal panel, how to remove this resist is explained.

[0044]First, the lid 2 is opened in order to put the glass substrate of the liquid

crystal panel which is the washed object 3 into the resisting pressure tub 1 (drawing 2 (a)). The glass substrate in which the resist which is an organic high polymer substance for removal has adhered to the surface is stored in the resisting pressure tub 1 (drawing 2 (b)), and the lid 2 is shut (drawing 2 (c)). Two or more sheets are arranged in the resisting pressure tub 1, glass substrates keep a certain amount of interval, and a glass substrate is put in order so that the field where resist is applied may become vertical to the bottom of the resisting pressure tub 1.

[0045]Next, the valve 5 is opened wide and the carbon dioxide which is a gas is poured into the resisting pressure tub 1 from the bomb 4. The compressor 6 is operated and pressure up is carried out until the pressure in the resisting pressure tub 1 reaches 5MPa. The valve 5 will be closed if the pressure in the resisting pressure tub 1 is set to 5MPa with carbon dioxide (drawing 2 (d)).

[0046]Next, operation of the high pressure pumping 8 is started (drawing 2 (e)), and the water which is a fluid is sent out to the high pressure pumping 8 from the solvent tank 7 by opening the valve 9. A pressure heats the water used as 5.1MPa to through and 200 °C to the heater 10 by going via the high pressure pumping 8.

[0047]An ammonia solution is mixed in 5.1MPa and the water used as 200 °C, i.e., the water of a subcritical state, as a removal acceleration component. The ammonia solution stored in the removal acceleration component tank 12 is mixed by the water which pressure up was carried out with the high pressure pumping 13, and was heated with the heater 10 through the valve 14 (drawing 2 (f-2)). The water of a subcritical state with which the ammonia solution was mixed is mixed towards a glass substrate through the nozzle 11 (drawing 2 (f-1)).

[0048]Although the removing time of the resist when completely not mixing an ammonia solution is 10 minutes, when an ammonia solution is mixed so that it may become water of a subcritical state with 10 ppm, it is 5 minutes, and the removing time of resist can be shortened.

[0049]As said removal acceleration component, fluoric acid solution, a hydrochloric acid aqueous solution, a nitric acid solution, phosphoric acid solution, hydrogen peroxide solution, etc. besides an ammonia solution may be used. Although the water of the subcritical state is used as a fluid which mixed to a glass substrate, the water of a supercritical state may be sufficient. It is not necessary to make the water of a subcritical state mix said removal acceleration component depending on the case.

[0050]Here, the state where the both sides of the critical pressure peculiar to a substance and critical temperature were exceeded is pointed out, and, as for a supercritical state, a subcritical state refers to the state where 1/5 of the critical pressure peculiar to a substance and one fifth of the both sides of critical temperature were exceeded. The critical pressure of water is 22.1MPa and critical temperature is 374 °C.

[0051]Compared with a gas, density is large, since the fluid of a subcritical state thru/or a supercritical state has small viscosity compared with a fluid, it permeates the detailed portion of a glass substrate easily, and its reactivity is also high. Therefore, the resist on a glass substrate is cheaply removable by using the water of a subcritical state as a fluid.

[0052]The water of the subcritical state which filled up the resisting pressure tub 1 with carbon dioxide, and mixed the ammonia solution by mixed to a glass substrate so that it may mention above. While resist is physically removable with a mixed pressure, resist is chemically removable by the dissolution or decomposition



by water of said subcritical state (drawing 2 (g)).

[0053] Since it is \*\*\*\*(ed) to the resisting pressure tub 1 like conventional technology rather than filling the water of a subcritical state, the water of a reactant high subcritical state does not contact the wall of the resisting pressure tub 1 for a long time, and a glass substrate is not polluted with a metal impurity, organic impurities, etc. which are eluted from the resisting pressure tub 1.

[0054] In conventional technology, a fluid is made into the elevated temperature and high voltage from which a fluid will be in a subcritical state thru/or a supercritical state with the high pressure pumping 8 and the heater 10, and it is necessary to feed to the resisting pressure tub 1 until a fluid reaches conditions required for removal of an organic high polymer substance. However, since there is a limit in the liquid-sending capability of the high pressure pumping 8, a long time is required for filling a hot and high-pressure fluid to the resisting pressure tub 1. Therefore, to raise the pressure of a fluid for a short time, it is necessary to enlarge capability of the high pressure pumping 8 and the heater 10.

[0055] On the other hand, a hot and high-pressure fluid is not filled with this invention in large quantities to the resisting pressure tub 1, but a fluid is \*\*\*\*(ed), and it applies to a washed object. That is, since an organic high polymer substance is removed by carrying out every pressure powder of a little fluids [ some of ] of an elevated temperature and high voltage to the resisting pressure tub 1 with which the gas of the predetermined pressure was filled up beforehand, it is not necessary to make a lot of fluids into an elevated temperature and high voltage, and to feed them at once. Therefore, it is not necessary to enlarge capability of the high pressure pumping 8 and the heater 10, time to start the pressure buildup of a fluid can be shortened, and a tact time required for processing can be shortened.

[0056] If the processing time of the conventional removing method at the time of actually using the pump of the same liquid-sending capability and the removing method in this invention is compared, it is about about 10 times as many differences, and according to the removing method in this invention, processing time can be shortened substantially.

[0057] As the nozzle 11, the slit nozzle which \*\*\*\* a fluid in layers is used. Two or more these slit nozzles are arranged so that it may become parallel to a glass substrate, for example. Since the slit nozzle can \*\*\*\* a fluid in layers, cannot scatter easily around and does not require the water of a subcritical state for the wall of the resisting pressure tub 1 easily when the water of a subcritical state is \*\*\*\*(ed) to a glass substrate, its effect of preventing the corrosion of the resisting pressure tub 1 is high.

[0058] As the nozzle 11, the spraying nozzle which \*\*\*\* a fluid to misty state, the shower nozzle which \*\*\*\* a fluid in the shape of [ of a single flat surface ] a sector film, etc. may be used. These nozzles have a high effect which reduces the amount of \*\*\*\* of a fluid. The effect of a shower nozzle of physical removal of the resist by the high voltage shower washing using the \*\*\*\* pressure of the fluid is high. The nozzle mentioned above may be used independently and may be used together.

[0059] The difference of the pressure of the water \*\*\*\*(ed) from the nozzle 11 and the pressure in the resisting pressure tub 1 is below 490kPa (5kgf/cm<sup>2</sup>) preferably. If setting a pressure differential to 490 or less kPa has a pressure differential larger than 490kPa, when removing the resist on the glass substrate which breaks easily, it is because it becomes easy to damage a glass substrate with a \*\*\*\*

pressure.

[0060]Next, the pressure control valve 15 is passed, and the water of the subcritical state having contained the removed resist is discharged from the resisting pressure tub 1, and is collected to the decompression container 16 (drawing 2 (h)). Discharge from the resisting pressure tub 1 of the water of this subcritical state is performed in parallel to \*\*\*\* of the water of the subcritical state to a glass substrate.

[0061]As a method of promoting the discharge to the decompression container 16, a pressure differential or the difference of elevation is provided between the resisting pressure tub 1 and the decompression container 16, and the method of using them and the method of making the resisting pressure tub 1 incline are mentioned. This method may be used independently and may be used together.

[0062]In order that the carbon dioxide in the resisting pressure tub 1 may fall out from the pressure control valve 15 continuously at this time, the pressure in the resisting pressure tub 1 is maintained at 5MPa by opening the valve 5 wide and sometimes sending carbon dioxide into the resisting pressure tub 1.

[0063]Since the fluid in which reactivity increased is filled with conventional technology to the resisting pressure tub 1 as stated even in the top, the metallic material of the wall of the resisting pressure tub 1 may be melted, and the washed object 3 may be polluted with the eluted metallic material. The contamination by the metal in which especially the washed object 3 is eluted in the case of the glass substrate of a semiconductor and a liquid crystal panel, etc. gives a fatal damage to the yield of a product. For example, even when SUS316L which is a charge of a stainless steel material is used as a material of the resisting pressure tub 1 and a stable oxide film is formed in the surface, the surface is corroded at about 0.1 mm/day in speed. The metal which was corroded and was eluted adheres to a glass substrate, and stops accomplishing the business as a glass substrate of a liquid crystal panel. In this invention, this problem is solved, and since the water of a subcritical state is not made to stagnate in the resisting pressure tub 1 for a long time but is discharged promptly, said contamination does not take place.

[0064]Since the water collected by the decompression container 16 separates from the temperature and the pressure conditions which were given by the resisting pressure tub 1, the removal performance of resist is lost quickly and the organic substance removed in the decompression container 16 deposits. When a fluid is water of a subcritical state, the decomposition reaction of resist occurs preferentially and a with a molecular weight [ with benzene skeletons ] of about 100 to 200 organic substance deposits.

[0065]The supernatant water in the decompression container 16 is discharged to the solvent liberating tank 17 using the difference of elevation or a pump, and is again used as a fluid of resist removal through waste water treatment equipments (not shown), such as activated carbon, ion-exchange resin, bio-processing, UV disinfection, and a semipermeable membrane, a water purifying apparatus (not shown), etc.

[0066]Since heat occurs by the decomposition reaction of resist in spite of \*\*\*\* (ing) the water of the subcritical state which are 5.1MPa and 200 \*\* to the glass substrate, the resist surface temperature on a glass substrate amounts to 220 \*\*. This is used and the end time of a removal reaction is judged by measuring the temperature change on the surface of a glass substrate, the temperature change of the water of a subcritical state which finished reacting, etc. The end time of this removal reaction may be judged by measuring the pressure variation of the water of

a subcritical state. That is, while the removal reaction is progressing continuously, the pressure in the resisting pressure layer 1 continues rising. If a removal reaction approaches an end, the increasing rate of the pressure in the resisting pressure layer 1 decreases. As mentioned above, in order to make regularity the pressure in the resisting pressure layer 1 which decreases by discharging the water of a subcritical state from the resisting pressure layer 1, the valve 5 is opened wide, carbon dioxide is sent into the resisting pressure layer 1, and the pressure in the resisting pressure layer 1 is maintained at 5MPa. Therefore, in the interval from opening of this valve 5 to opening of the following valve 5, compared with the early stages of a reaction, the direction of the telophase of a reaction becomes narrow. The end time of a removal reaction is judged using this.

[0067]Next, after the water of the subcritical state \*\*\*\*(ed) from the nozzle 11 finishes removing resist from a glass substrate, it closes the valve 9 and the valve 14, stops \*\*\*\* of the water of a subcritical state (drawing 2 (i)), and suspends a resist removal reaction (drawing 2 (j)).

[0068]Next, after fully discharging the water of a subcritical state from the resisting pressure tub 1, the opening of the pressure control valve 15 is changed and the pressure of the resisting pressure tub 1 is decompressed even to atmospheric pressure (drawing 2 (k)). A glass substrate is quenched by the adiabatic expansion by reducing the pressure in the resisting pressure tub 1 rapidly. It may dew, if the lid 2 is opened and a glass substrate is taken out as it is. In order to prevent this, the heating nitrogen made by the heating gas manufacturing installation 19 is injected to a glass substrate through the valve 18 (drawing 2 (l)).

[0069]In order to inject heating gas uniformly at this time, a nozzle may be provided inside the resisting pressure tub 1, and it may connect with the valve 18. By using this nozzle, the amount of the nitrogen used is made in half. In the embodiment of this invention, although heating nitrogen was used, other gas may be used.

[0070]With heating nitrogen, if a glass substrate is warmed more than the dew point, the lid 2 will be opened and a glass substrate will be taken out (drawing 2 (m)).

[0071]Although an expensive solvent and ozone must be used for resist removing and expenses, such as flue gas treatment, solvent purchase, and solvent treatment, are needed for it in the former, Since cheap water is used as a fluid and special processing is not needed, either, when the removing method of the organic high polymer substance of this invention is used with the resist removing device of a liquid crystal panel manufacturing installation as mentioned above, with this device, resist removing can be performed cheaply.

[0072]Although the embodiment mentioned above explained the case where the removing method of the organic high polymer substance of this invention was used with the resist removing device of a liquid crystal panel manufacturing installation, it may use with the resist removing device in a semiconductor substrate manufacturing installation, a solar cell manufacturing installation, an opto device manufacturing installation, etc.

[0073]Although the case where the resist applied to the glass substrate which is the washed object 3 was removed was described, even if the washed objects 3 are works (a semiconductor wafer, a glass material, a ceramic material, etc.) other than a glass substrate, a jig, a tool, a device, etc., they can apply this

invention.

[0074]As resist for removal, even when removing not only novolac type photoresist but negative-mold novolak resin resist, positive type rubber system resist, etc., the same result is obtained. Reaction time changes with the coating weight of resist, curing conditions, impurity quantity, leaving times, organic components, etc.

[0075]As a candidate for removal, even if it is dioxin, PBC, activated sludge, and other organic high polymer substances, this invention is applicable.

[0076]As a fluid, the polar solvent of not only water but a subcritical state thru/or a supercritical state may be used. A pressure and temperature are higher than atmospheric pressure and a room temperature, and as long as the density is a fluid which is more than  $0.1 \text{ g/cm}^3$ , it may use as a fluid in this invention.

[0077]The same result is obtained, even if the polar solvent which dissolves in water, such as methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, acetic acid, phenol, and DMSO (dimethyl sulfoxide), is mentioned and it uses these as said polar solvent. Unlike the case where water is used, at this time, processing time, temperature, a pressure, etc. serve as conditions peculiar to each polar solvent. The case where a decomposition reaction occurs preferentially depending on the kind of polar solvent to be used, and lytic reaction may occur preferentially. For example, when DMSO is used for a fluid, lytic reaction occurs preferentially.

[0078]Although the carbon dioxide which is inactive gas was used in the embodiment mentioned above as a gas with which the resisting pressure tub 1 is filled up, other inactive gas may be used.

[0079]

[Effect of the Invention]As mentioned above, according to this invention, since it is not necessary to fill a reactant high fluid in a resisting pressure tub and this fluid does not contact the wall of a resisting pressure tub for a long time, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented. Since it is unnecessary although a fluid is fed with high pressure pumping for a long time until a fluid reaches conditions required for removal of an organic high polymer substance, time to start the pressure buildup of a solvent can be shortened and a tact time required for processing can be shortened.

[0080]According to this invention, removal of organic high polymer substances, such as resist adhering to works, such as a semiconductor wafer, a glass material, or a ceramic material, can be performed.

[0081]Since said fluid is a polar solvent of the water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state according to this invention, this fluid tends to diffuse the inside of a substance, and permeates the detailed portion of a washed object easily. Therefore, an organic high polymer substance can be removed more certainly in a short time. Since water and a polar solvent are cheap, the removal cost of an organic high polymer substance can be held down.

[0082]According to this invention, since said gas is inactive gas, it has not said that a washed object and a chemical reaction are caused, and is easy also for handling. Since inactive gas is cheap, the removal cost of an organic high polymer substance can be held down.

[0083]Since said nozzle is used according to this invention, it can \*\*\*\* efficiently towards a washed object and a fluid cannot scatter easily to the wall

of a resisting pressure tub. Therefore, since this fluid does not contact the wall of a resisting pressure tub for a long time, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented. Since the pressure of the fluid concerning the washed object by \*\*\*\* is strong, an organic high polymer substance can be removed more certainly.

[0084]According to this invention, since the removal acceleration component which carries out promotion of removal of an organic high polymer substance to a fluid is added, removal of the organic high polymer substance adhered or welded can be ensured in a short time. Therefore, the removing time of an organic high polymer substance can be shortened.

[0085]According to this invention, since temperature up of the washed object is carried out by the heated gas before taking out a washed object from a resisting pressure tub, after decompressing the inside of a resisting pressure tub, the dew condensation produced when taking out a washed object from a resisting pressure tub can be prevented.

[0086]According to this invention, since the fluid which the removed organic high polymer substance mixed is discharged from a resisting pressure tub in parallel to \*\*\*\* of a fluid, the fluid having contained the organic high polymer substance removed from the washed object does not collect in a resisting pressure tub, and this fluid does not contact the wall of a resisting pressure tub for a long time. Therefore, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented.

[0087]According to this invention, since the pressure differential with the fluid by which twist pressure powder is carried out to the gas with which the resisting pressure tub was filled up by said gas restoration means, and said hydrostatic pressure powder means is 490 or less kPa, it can remove an organic high polymer substance, without damaging a washed object by the power by \*\*\*\*.

[0088]Since the stage which removal of the organic high polymer substance adhered or welded ended is judged to a washed object using at least one among the temperature change of the surface of a washed object, the pressure variation of a fluid, and the temperature change of a fluid according to this invention, The stage which removal of the organic high polymer substance adhered or welded ended can be judged correctly. Therefore, removal of an organic high polymer substance can be ensured.

[0089]According to this invention, by the process of \*\*\*\*(ing) a fluid to the washed object in a resisting pressure tub, since the organic high polymer substance adhered or welded [ said ] is removed, it is not necessary to fill a reactant high fluid in a resisting pressure tub, and this fluid does not contact the wall of a resisting pressure tub for a long time. Therefore, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented. Although a fluid is fed with high pressure pumping for a long time, it is unnecessary until a fluid reaches conditions required for removal of an organic high polymer substance. Therefore, time to start the pressure buildup of a solvent can be shortened and a tact time required for processing can be shortened.

[0090]According to this invention, since the pressure in said resisting pressure tub is decompressed to atmospheric pressure in order to take out said washed object from which the organic high polymer substance was removed from said resisting pressure tub, a washed object can be taken out safely from a resisting pressure

tub.

[0091]According to this invention, since the fluid which the organic high polymer substance removed by \*\*\*\*(ing) a fluid mixed is discharged from said resisting pressure tub, the fluid which the organic high polymer substance removed in the resisting pressure tub mixed does not collect in this resisting pressure tub, and this fluid does not contact the wall of a resisting pressure tub for a long time. Therefore, contamination of the washed object by a metal impurity, organic impurities, etc. which are eluted from a resisting pressure tub can be prevented.

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[Translation done.]

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CLAIMS

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[Claim(s)]

[Claim 1] A stripper of an organic high polymer substance characterized by comprising the following which removes physically and chemically an organic high polymer substance which used a fluid, and was adhered or welded.

A resisting pressure tub for storing said washed object and removing said organic high polymer substance.

A gas restoration means to fill up this resisting pressure tub with a gas of a predetermined pressure.

A hydrostatic pressure powder means to \*\*\*\* a fluid of a predetermined temperature by a pressure more than said predetermined pressure to a washed object of this resisting pressure tub.

[Claim 2] A stripper of the organic high polymer substance according to claim 1, wherein said washed object is a semiconductor wafer, a glass material, or a ceramic material.

[Claim 3] A stripper of the organic high polymer substance according to claim 1, wherein said fluid is a polar solvent of water of a subcritical state thru/or a supercritical state or a subcritical state thru/or a supercritical state.

[Claim 4] A stripper of the organic high polymer substance according to claim 1, wherein said gas is inactive gas.

[Claim 5] In said hydrostatic pressure powder means, fluid rocket engine jets for \*\*\*\*(ing) a fluid. A stripper of the organic high polymer substance according to any one of claims 1 to 4 using at least one of a slit nozzle which \*\*\*\* a fluid in layers, a spraying nozzle which \*\*\*\* a fluid to misty state, and shower nozzles which \*\*\*\* a fluid in the shape of a fanning film.

[Claim 6] A stripper of the organic high polymer substance according to any one of claims 1 to 5, wherein said hydrostatic pressure powder means includes a removal acceleration component adding means which adds a removal acceleration component of said organic high polymer substance.

[Claim 7] A stripper of the organic high polymer substance according to claim 1 including a washed object heating method which carries out temperature up of the washed object in a resisting pressure tub by flowing heated gas.

[Claim 8] A stripper of the organic high polymer substance according to claim 1 including a fluid discharge means which discharges a fluid which an organic high polymer substance removed by said hydrostatic pressure powder means mixed from a resisting pressure tub in parallel to \*\*\*\* of a fluid by said hydrostatic pressure powder means.

[Claim 9]A stripper of the organic high polymer substance according to claim 1, wherein a pressure differential of a gas with which a resisting pressure tub was filled up by said gas restoration means, and a fluid by which twist pressure powder is carried out to said hydrostatic pressure powder means is 490 or less kPa.

[Claim 10]A stage which removal of an organic high polymer substance adhered or welded ended, A stripper of the organic high polymer substance according to any one of claims 1 to 9 containing a means to judge using at least one among a temperature change of the surface of a washed object, pressure variation of a fluid, and a temperature change of a fluid.



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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is a schematic diagram of the stripper 30 of the organic high polymer substance which is one gestalt of operation of this invention.

[Drawing 2] It is process drawing showing the removing method of the organic high polymer substance which are other gestalten of operation of this invention.

[Description of Notations]

- 1 Resisting pressure tub
- 2 Lid
- 3 Washed object
- 4 Bomb
- 5, 9, 14, and 18 Valve
- 6 Compressor
- 7 Solvent tank
- 8, 13 high pressure pumping
- 10 Heater
- 11 Nozzle
- 12 Removal acceleration component tank
- 15 Pressure control valve
- 16 Decompression container
- 17 Solvent liberating tank
- 19 Heating gas manufacturing installation

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[Translation done.]

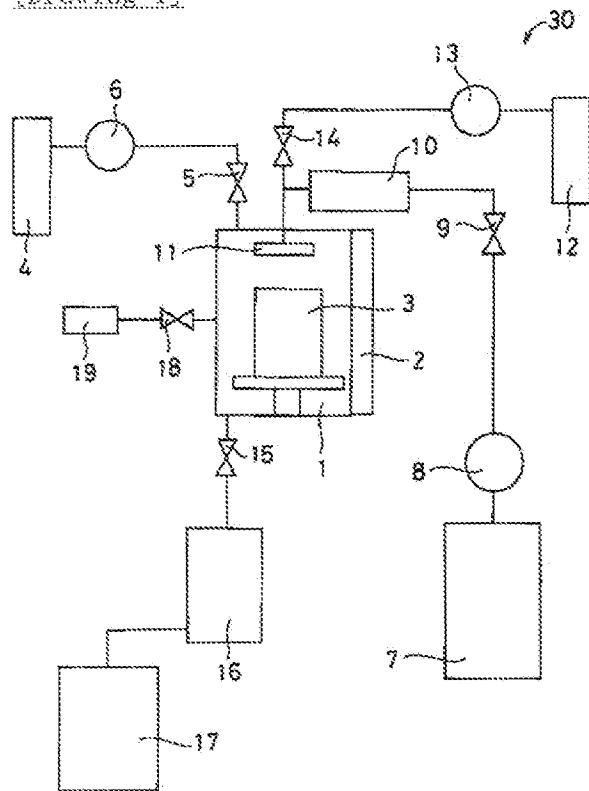
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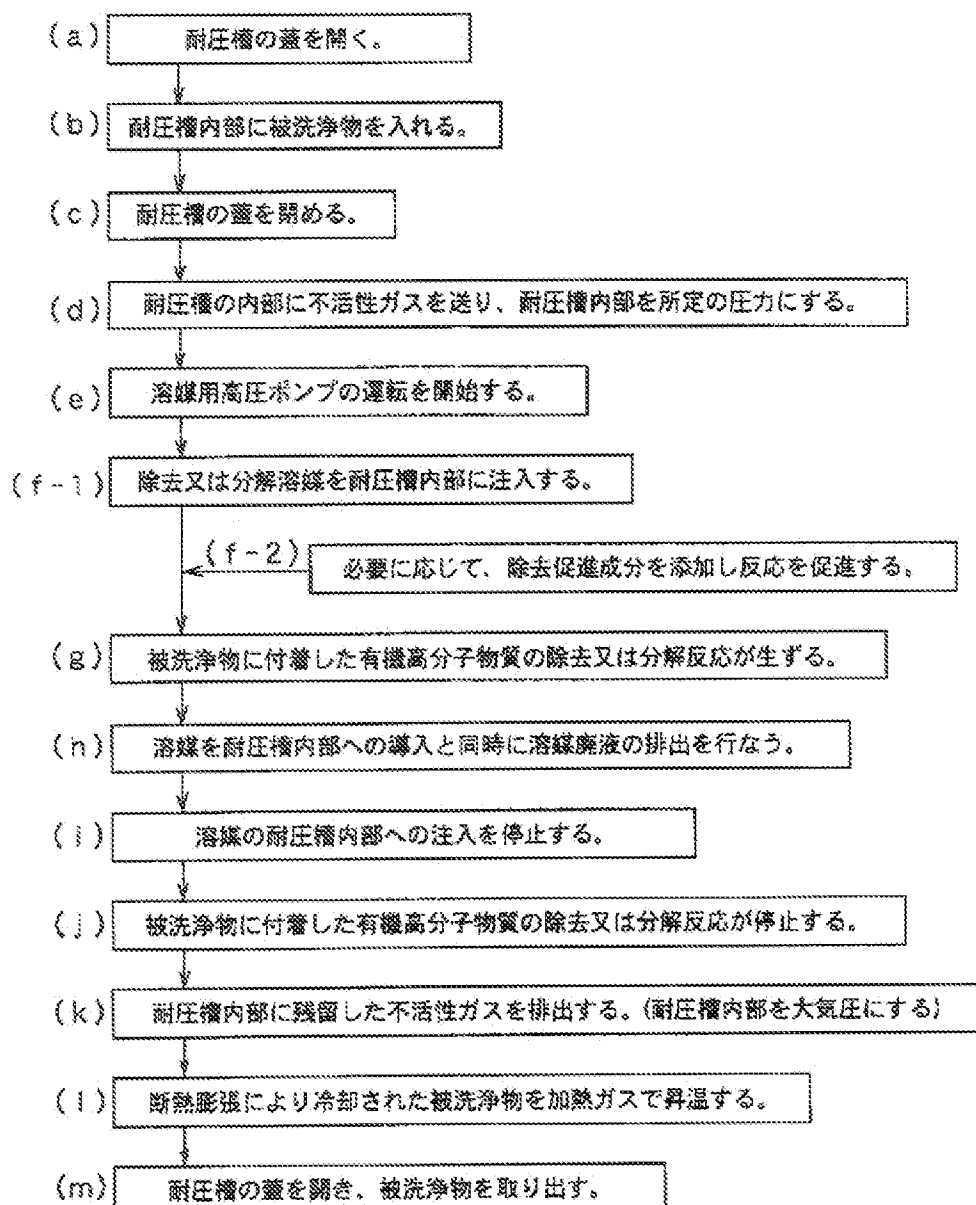
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## DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]